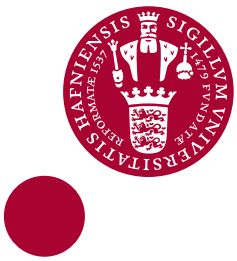

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Jahn-Teller beads on a string: Synthesis and magnetic properties of one-dimensional fluoride-bridged manganese(III)-systems

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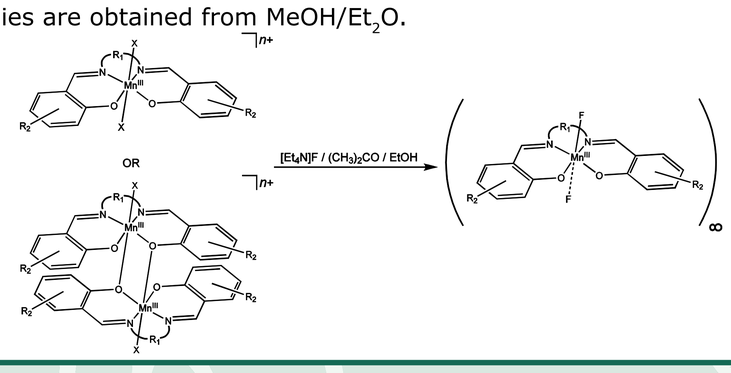
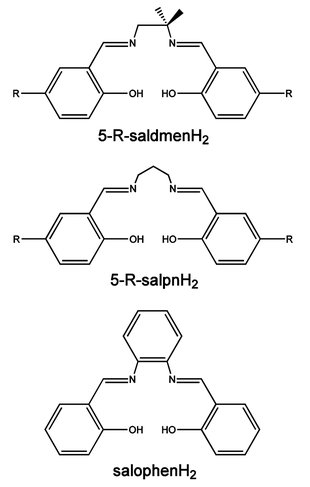
Introduction

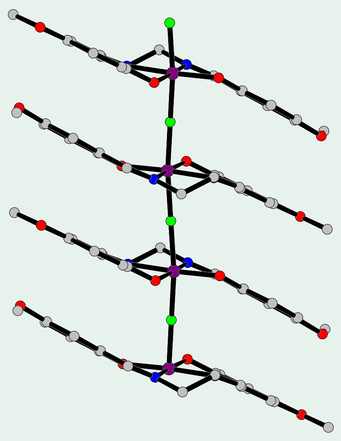
The system *catena*-[Mn^{III}(F)(salen)] ($salenH_2$ = *N*,*N*'-bis(salicylidene)ethylenediamine), as published by Birk *et al*., [1], presented the first example of a fluoride-bridged chain based on the ubiquitous [Mn^{III}(salen)]$^+$-unit. To expand this class of compounds, a new and more general route to *catena*-[Mn(F)(Schiff base)]-systems has been developed. By varying the Schiff base ligand, systems with both strictly linear bridges as in *catena*-[Mn^{III}(F)(5-MeO-salen)]·½MeOH·½H_2O (**1**), somewhat bent bridges as in *catena*-[Mn^{III}(F)(5-Me-saldmen)]·MeOH (**2**) (164°), and even quite bent bridges as in *catena*-[Mn^{III}(F)(salpn)] (**3**) (146°) and *catena*-[Mn^{III}(F)(5-MeO-salpn)] (**4**) (144°), have been synthesized. In these compounds, the Jahn-Teller axis is along the Mn-F bonds, providing sufficient basicity of the fluoride ligand to make fluoride-bridging the structure-directing motif. Sizeable antiferromagnetic intrachain exchange interactions are found in all the compounds, emphasizing the potential of fluoride as a good mediator of magnetic exchange interaction in polynuclear complexes. By tuning the bridging angle and crystal packing, interesting magnetic properties arise, and in **3**, slow relaxation of the magnetization is observed. The slow relaxation is a result of a small canting of the spins on neighboring manganese(III)-centers in the chains.

Synthesis

The synthetic protocol published for *catena*-[Mn^{III}(F)(salen)], [1], fails upon sufficient modification of the Schiff base type ligand. Instead *catena*-[Mn^{III}(F)(Schiff base)] systems can be prepared by addition of fluoride to [Mn^{III}(Schiff base)X_2]$^{n+}$ or [Mn^{III}_2(Schiff base)$_2X_2$]$^{n+}$ precursors (X = solvent molecules or triflate counterions) in acetone/ethanol binary solvents. Crystals suitable for single crystal X-ray diffraction studies are obtained from MeOH/Et_2O.





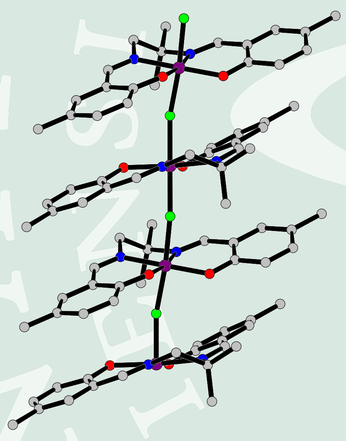


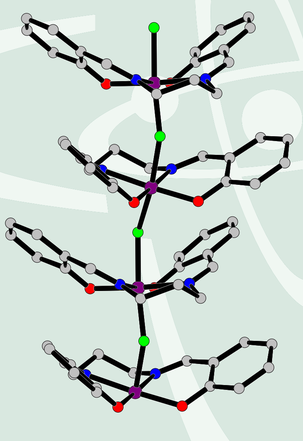
1
Space group: *P*-1
Mn-F-Mn = 180.00°
F-Mn-F = 169.99°
Mn-F = 2.0318 Å and 2.0329 Å

Brown blocks

Light brown needles

Space group: $P2_1/c$
Mn-F-Mn = 163.61°
F-Mn-F = 174.08°
Mn-F = 2.0678 Å and 2.0731 Å
2



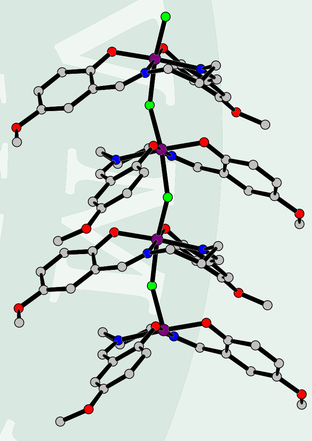


Space group: $P2_1/m$
Mn-F-Mn = 143.52° and 144.21°
F-Mn-F = 167.60° and 168.28°
Mn-F = 2.0557 Å, 2.0588 Å, 2.0859 Å and 2.0927 Å
4

Dark green needles

Greenish brown needles

Space group: $P2_12_12_1$
Mn-F-Mn = 145.82°
F-Mn-F = 167.86°
Mn-F = 2.0530 Å and 2.0856 Å
3



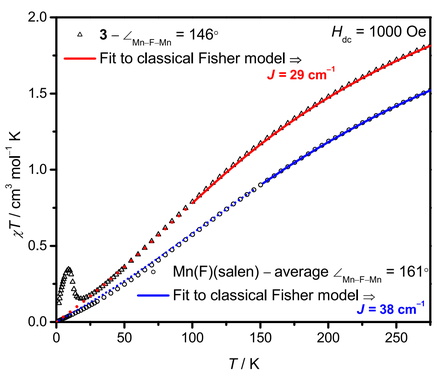
Magnetic hysteresis behavior of 3

In **3**, the bending of the fluoride bridges weakens the antiferromagnetic exchange interaction between neighboring manganese(III)-centers, as evident from the fitting of the static magnetic susceptibility data to the isotropic Heisenberg Hamiltonian:

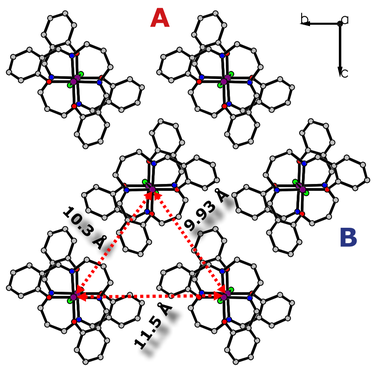
$$\hat{H} = J\sum_i \hat{S}_i \cdot \hat{S}_{i+1} + \mu_B g B \sum_i \hat{S}_i \qquad (1)$$

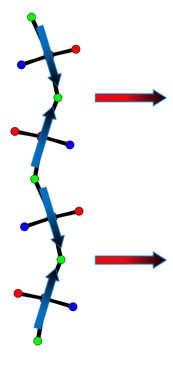
by use of the classical Fisher expression for the magnetic susceptibility of an infinite chain of classical spins, [2]:

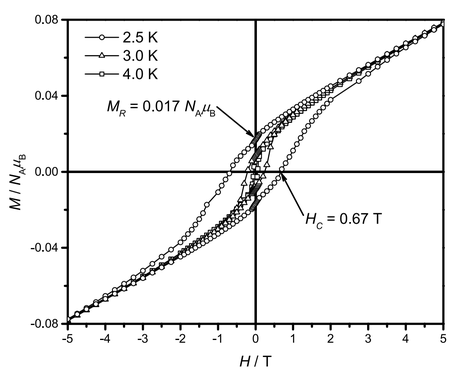
$$\chi = \frac{N_A g^2 \mu_B^2 S(S+1)}{3kT}\frac{1+u}{1-u} \quad , \quad u = \left(\frac{kT}{S(S+1)J}\right) - \coth\left(\frac{S(S+1)J}{kT}\right)$$



The chain motif is generated by 2_1 screw axes, making neighboring manganese(III)-centers magnetically inequivalent as well as generating two magnetically inequivalent chains within the unit cell, **A** and **B**. Due to the large local axial anisotropy ($D \sim -3.5$ cm^{-1}), each manganese(III)-center has a preferred orientation of the magnetization, ➡. From magneto-structural considerations regarding the size of *J*, *D* and the angle between the easy axes and the chain axis, [3], a canting angle of 1.4° is calculated, meaning that each chain has a small uncompensated magnetic moment perpendicular to the chain, ➡. Below *T* = 8 K a phase transition to a phase showing magnetic bistability occurs, with the opening of a hysteresis loop at *T* = 4 K.

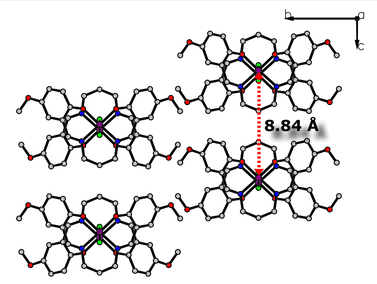


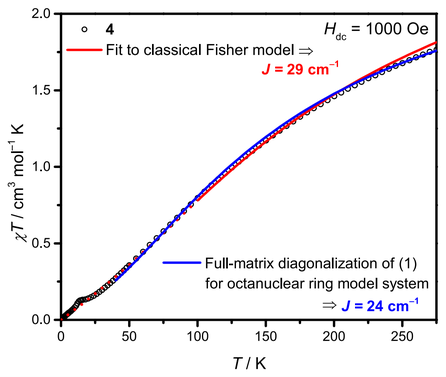


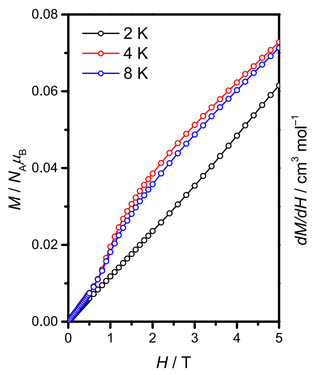


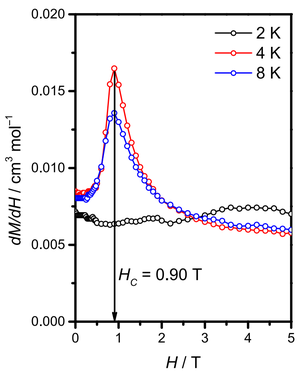
Antiferromagnetic ordering in 4

In **4**, a substantial antiferromagnetic intrachain exchange interaction is found, and following similar considerations as for **3**, an uncompensated magnetic moment perpendicular to the chains is expected. From maxima in the numerical field derivative of the magnetization and the low-temperature magnetic susceptibility, a transition to an antiferromagnetically ordered phase with T_N = 13 K and H_C = 0.90 T is concluded. The unusual behavior of *M* at *T* = 2 K might be a result of a transition to a structural phase with much stronger interchain interactions.



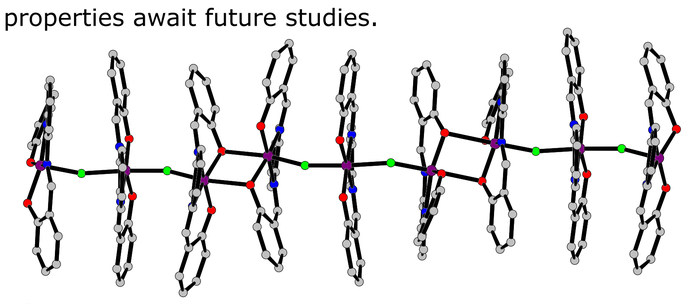


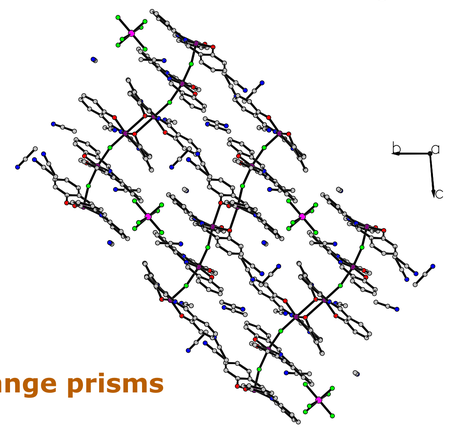




A different kind of chain

The reaction between [Mn^{III}(salophen)(CF_3SO_3)] and [$Re^{IV}F_6$]$^{2-}$ yields a fluoride-bridged one-dimensional manganese(III) coordination polymer, consisting of both mononuclear [Mn^{III}(salophen)]$^+$-units and [Mn^{III}_2(salophen)$_2$]$^{2+}$ out-of-plane dimers, with octahedral [$Re^{IV}F_6$]$^{2-}$ counterions neutralizing the charge of the chains. The fluoride linkers are believed to stem from a possibly redox promoted fluoride abstraction from the otherwise robust hexafluoridorhenate(IV). The magnetic properties await future studies.



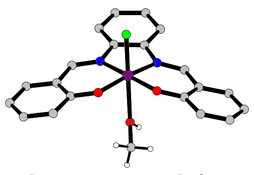


Space group: *P*-1
F-Mn-F = 156.67° and 164.44°
Mn-F = 1.9836 Å, 1.9955 Å, 2.0721 Å and 2.1156 Å
$(Mn\cdots Mn)_{out\text{-}of\text{-}plane\ dimer}$ = 3.259 Å and 3.349 Å

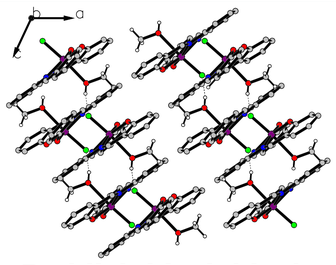
Dark orange prisms

A mononuclear exception

If the general synthetic procedure is followed with [Mn^{III}(salophen)(CF_3SO_3)] as precursor, the outcome is the mononuclear complex *trans*-[Mn^{III}(F)(MeOH)(salophen)]. The complex forms a one-dimensional network through O-H···F hydrogen-bonding.



Space group: $P2_1/n$
F-Mn-O_{MeOH} = 175.39°
Mn-F = 2.0546 Å
Mn-O_{MeOH} = 2.4289 Å



Reddish black blocks

Conclusions

This work shows the versatility of fluoride as bridging ligand, and therefore structure-directing motif, in polynuclear coordination compounds. The fluoride ligand mediates relatively strong magnetic exchange interaction with $J_{Mn\text{-}Mn}$ ~ 25 - 40 cm^{-1}. Through minor structural changes, *e.g*. tuning of the bridging angle, systems with highly different properties can be constructed.

References

[1] Birk, T.; Pedersen, K. S.; Piligkos, S.; Thuesen, C. A.; Weihe, H.; Bendix, J., *Inorg. Chem.*, **2011**, *50*, 5312. [2] Fisher, M. E., *Am. J. Phys.*, **1968**, *32*, 343. [3] Mossin, S.; Weihe, H.; Sørensen, H. O.; Lima, N.; Sessoli, R., *Dalton Trans.*, **2004**, 632.

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